

LABNOTES

Fall 1998



The Newsletter of the Wisconsin Laboratory Certification and Registration Program
Program Information: (608) 267-7633 Program Fax: (608) 266-5226

NELAC technical advisory committee recommends DNR seek national accreditation

Alfredo Sotomayor, Senior Audit Chemist

In early 1998, the Wisconsin Department of Natural Resources convened a technical advisory committee (TAC) to seek advice on how to proceed with adopting the National Environmental Laboratory Accreditation Conference (NELAC) standards in Wisconsin. The committee finalized its recommendations at its last meeting on July 21, 1998. The TAC met six times and its members represented the breadth of environmental laboratory types and data users in Wisconsin.

The NELAC technical advisory committee recommended that the DNR seek recognition from the National Environmental Laboratory Accreditation Program as an accrediting authority. The committee also recommended that not all Wisconsin laboratories be accredited under the NELAC standards. In essence, the TAC recommended maintaining a two-tiered accreditation system. The profit status and the type of testing performed at a facility would be used to determine which laboratories will be required to be accredited under NELAC or *certified* under chapter NR 149, Wis. Adm. Code. The emphasis on the word "certified" is deliberate. The TAC recommended eliminating the current registration option for laboratories that do not perform work for hire.

The committee is completing a report of its activities that should be available in late October. The laboratory certification pro-

gram intends to post the report on its web site (see page 2). The next steps for the program involve seeking endorsements from the Laboratory Certification Standards Review Council and concurrence from DNR Administration and the Natural Resources Board. If the Department proceeds with adoption of the NELAC standards, chapter NR 149, Wis. Adm. Code, would need to be amended through the normal notice and comment rule-making procedures, which gives all affected parties an opportunity for input. For more information about the technical advisory committee, please contact Alfredo Sotomayor at (608) 266-9257.

In This Issue...

- 2 Summary of TAC recommendations
- 3 DNR releases updated "Yellow Book"
- 3 SLH offers drinking water PT samples
- 4 Reference sample update
- 4 Getting enough sample volume for MS/MSD
- 6 Federal Regulations Update
- 9 DNR accepting nominations for lab of the year
- 10 Year 2000 compliance for laboratories
- 10 Requirements for hexane extractable material
- 11 Council Corner
- 12 DNR implements dissolved-based limits
- 13 DNR investigates MDLs, report forthcoming
- 15 Determining the LDR for metals analysis
- 16 The Auditor's Corner
- 19 Required certifications for haz. waste tests
- 21 Wastewater Lab Forum
- 23 NELAC IV: moving towards implementation
- 24 DNR phases in new permit applications

Summary of advisory committee recommendations

The NELAC technical advisory committee made the following specific recommendations:

- DNR should seek recognition as an accrediting authority from NELAP.
- All laboratories performing work “for profit” would be accredited under the NELAC standards.



LabNotes - Newsletter of the Laboratory Certification Program

LabNotes is published twice annually by the Wisconsin DNR laboratory certification and registration program. For information about distribution or to make suggestions for future articles, contact the editor at (608) 267-0579.

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This newsletter is intended to present current information and issues to certified and registered laboratories. This newsletter does not establish policy for the Department.

- “Not for profit” laboratories that perform sophisticated tests (not titrimetric, not by ion selective electrode) beyond those currently covered by test categories 1 through 4 would also be accredited under the NELAC standards.
- Laboratories not in the NELAC group would be required to abide by the provisions currently applicable to certified laboratories under chapter NR 149, Wis. Adm. Code. These laboratories would also be able to join the NELAC group voluntarily.
- “Not for profit” laboratories would be required to file statements confirming their status. The committee recommended that there be oversight of this information.

Web Sites

Wisconsin Administrative Register
<http://www.legis.state.wi.us/rsb/code/register/>

National Technical Information Service:
<http://www.ntis.gov/>

NELAC
<http://www.epa.gov/ttn/nelac/>

USEPA
<http://www.epa.gov>

Wisconsin Revisor of Statutes
<http://www.legis.state.wi.us/rsb>

Wisconsin Laboratory Certification
<http://www.dnr.state.wi.us/org/es/science/lc/>

DNR releases updated “Yellow Book”

Jeffrey Ripp, Laboratory Certification Program

Earlier this fall, the Department of Natural Resources issued a new version of the *Laboratory Certification and Registration - Program Information and Requirements* document [DNR PUBL-TS-007-98]. This document is commonly called the “Yellow Book”. The August 1998 version (revision 7) of the Yellow Book has been completely reformat- ted, and includes the recent amendments to chapter NR 149, Wis. Adm. Code, which were published in the June 15, 1998 Wisconsin Administrative Register. The new Yellow Book expands upon previous versions by providing additional information about reference samples, on-site evaluations, applica- tions for certification and the DNR’s low- level data reporting requirement. The new version no longer contains the text of the administrative codes pertaining to wastewa- ter, safe drinking water, hazardous waste, groundwater, and spill site testing. The text of these rules was removed because it is now available on-line from the Wisconsin Revisor of Statutes web site at <http://www.legis.state.wi.us/rsb/>.

All currently certified and registered laboratories will receive one copy of this document. If your laboratory does not re- ceive a copy, please contact Jeff Ripp at (608) 267-0579 or by email at rippj@dnr.state.wi.us. The Department re- grets that it can only send one copy per fa- cility. If you would like additional copies, please consider downloading and printing the document from the laboratory certification program’s web site (see page 2).

★Please note that the tables in Sections 5 and 6 contain a typographical error. Tables 5.2, 5.5, 5.6, 5.7, 5.8, 5.9 and 6.2 list the units for MDLs, IDCs, PALs and MCLS as mg/L. This is incorrect. In each table, the units should be µg/L. See page 24 for details.

Hygiene Lab offers water supply PT samples

Jeffrey Ripp, Laboratory Certification Program

The Wisconsin laboratory certification program requires laboratories to analyze and pass a reference sample (a.k.a. proficiency testing sample) for each drinking water test annually. EPA will not offer water supply (WS) proficiency testing samples after 1998. Laboratories certified for safe drinking water testing will need to find an alternate refer- ence sample source to maintain their certifi- cation. Fortunately, a provider exists within the State of Wisconsin that can meet the re- quirements of the laboratory certification and registration program.

Starting in 1999, the Wisconsin State Laboratory of Hygiene will offer reference samples for the inorganic safe drinking water contaminants. The State Laboratory’s safe drinking water samples will be shipped three times a year; in January, April and September beginning with the E1-99 study in January 1999. These samples will be graded accord- ing to the criteria found in 40 CFR Part 141. Initially, the State Laboratory of Hygiene will offer four separate ampules, containing: (1) Metals (including all of the primary and secondary drinking water metals), (2) Cy- anide, (3) Sulfate and Fluoride, and (4) Ni- trate and Nitrite.

The State Laboratory of Hygiene oper- ates independently from the DNR and pre- pares reference samples specifically designed to meet the requirements of the Wisconsin laboratory certification program. For more information about these samples, contact Barb Burmeister of the State Laboratory of Hygiene at (608) 833-1770 ext. 107. Water supply samples are also available from Ana- lytical Products Group at (800) 272-4442 and Environmental Resource Associates at (800) 372-0122.

Reference sample update

EPA announces new requirements; NIST to certify providers

Mike Kvitrud, Laboratory Certification Program

Many changes are occurring in the world of reference samples. First, they are not even called reference samples anymore, but rather proficiency testing (PT) or performance evaluation (PE) samples. Second, the EPA will no longer maintain proficiency testing programs, leaving a void for many labs. Now that laboratories have completed their last EPA water supply (WS), water pollution (WP), or discharge monitoring report (DMR-QA) study, the DNR has been receiving calls concerning proficiency testing samples. One of the most common questions is “what does a lab need to do to continue its State of Wisconsin certification or registration?” Labs may continue using the approved suppliers listed in the “Yellow Book” (WDNR PUB-TS-007-98) to renew their Wisconsin certification or registrations. Labs which normally use the EPA samples to renew their Wisconsin certification or registration will now need to use one of the alternate suppliers.

The EPA will still require that labs and permittees participate in proficiency testing studies, but will no longer supply the proficiency testing samples. Instead, the National Institute of Standards and Technology (NIST) will accredit proficiency testing sample providers such as Environmental Resource Associates, Analytical Products Group, Analytical Standards Inc., and the Wisconsin State Laboratory of Hygiene to supply the samples for future studies. At this time, NIST has not accredited any suppliers. The first suppliers will be accredited some time after the first of the year. EPA will send out a WP, WS or DMR-QA study announcement as usual, but instead of sending samples, EPA will list the acceptable sources from which a lab may obtain the samples. The results from all of the acceptable provid-

ers will be reported to the EPA and to other regulatory agencies including the Wisconsin DNR.

In the near future, it may be possible to use one proficiency testing study to meet both federal and Wisconsin requirements. Until then, laboratories may still need to analyze a set of proficiency testing samples for the State of Wisconsin and a separate set for the EPA. If you would like more information about proficiency testing samples, please contact Jeff Ripp at (608) 267-0579 or by email at rippj@dnr.state.wi.us.

Matrix spike requirements: Is your lab getting enough sample volume?

Rick Mealy, Wisconsin Audit Chemist

One of the most frequent problems Wisconsin’s auditors encounter during evaluations is that laboratories are not meeting the required frequencies for matrix spikes and matrix spike duplicates (MS/MSD). Matrix spikes are prepared by adding a known amount of the compound of interest to real-world samples prior to extraction or other preparatory steps. Laboratories use matrix spikes to assess the effect of matrix interference on the recovery of chemicals in the sample. The frequency of matrix spikes and matrix spike duplicates is specified in many approved methods. If the frequency is not specified in the method, chapter NR 149, Wis. Adm. Code, states that:

*(Please see **Matrix Spikes** on page 5)*

(*Matrix Spikes*, from page 4)

“The frequency of spiked analysis shall be as cited in the approved method or authoritative source. If no frequency is given, then the minimum frequency shall be after the analysis of 10 samples, for test categories 10 to 17, 19, total organic halide and total organic carbon.”

Many laboratories have difficulty meeting the frequency requirement because they do not receive enough sample volume from their clients. When cited for not meeting the matrix spike/matrix spike duplicate frequency requirement, laboratories respond; “my clients simply don’t send enough bottles”. Unfortunate as it may seem, this is not an adequate response. Regardless of the amount of sample received, it remains the laboratory’s obligation to meet the frequency requirements for matrix spikes.

Laboratories seem to have the most difficulty meeting the 1 in 10 criteria for extractable organic tests (categories 11 and 12). These procedures require a full liter of volume for each sample and matrix spike pair. Ideally, a laboratory would receive three 1 liter samples collected during the same sampling event to prepare a sample, matrix spike, and matrix spike duplicate. This rarely occurs and laboratories have attempted to circumvent the frequency requirement by using other measures. A simple, but incorrect, solution adopted by many laboratories is to substitute “blank spikes” (laboratory control samples) for matrix spikes with each batch of samples. **For the purposes of certification in Wisconsin, analyzing laboratory control samples in lieu of matrix spikes/matrix spike duplicates is not an acceptable practice.** In other cases, laboratories may have two liters of sample available and use 1000 milliliters for the sample, and split the second liter into two 500 milliliter aliquots to prepare matrix spike and matrix spike duplicate. Again, this is not an acceptable practice because the matrix spikes con-

tain only 50% of the matrix effects present in the sample. This disparity can result in erroneous conclusions regarding sample-related matrix effects.

Laboratories need to work closer with environmental consultants and other clients to ensure that they receive sufficient sample volume to meet all their analytical and QA requirements. Until this occurs, the question remains: “What should a lab do if they do not receive enough sample to prepare one liter matrix spikes and matrix spike duplicates?” The DNR recommends that the laboratory split one liter of sample into three equal, 300-milliliter aliquots. Spike two of them and analyze each individually. This will result in elevated detection limits for that sample, which may confuse some clients. Each laboratory should make an effort to explain to its clients that this procedure is required for the laboratory to meet its obligations to the Wisconsin laboratory certification program. For more information about matrix spikes, please contact Rick Mealy at (608) 264-6006 or by email at mealyr@dnr.state.wi.us.

SW-846 requires matrix spikes for each analytical batch

Update III to SW-846 clarifies that matrix spikes must be performed with every set of 20 or fewer samples processed as a unit. This prohibits laboratories from extracting small numbers of samples each day to avoid preparing matrix spikes with each analytical batch. The bottom line is that if your laboratory extracts even a single sample, and that is all you plan to extract that day, you will need to extract a matrix spike and matrix spike duplicate along with the sample.


FEDERAL REGULATIONS UPDATE

SOLID & HAZARDOUS WASTE

EPA announces performance-based methods for RCRA monitoring

Proposed Rule, Federal Register, May 8, 1998

In the May 8, 1998 Federal Register, The U.S. Environmental Protection Agency (EPA) announced its intent to reform implementation of monitoring pursuant to the Resource Conservation and Recovery Act (RCRA) by formally adopting a performance-based measurement system in SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. This notice includes a proposal to change RCRA regulations so that the exclusive use of SW-846 methods will no longer be required. In this register, EPA also announced the availability of draft Update IVA to the Third Edition of SW-846, which contains new and revised methods. The comment period for this proposed rule closed on July 22, 1998. Proposed changes to SW-846 that may interest Wisconsin certified laboratories include deleting several individual methods and integrating them into comprehensive methods, removing chapter eleven from SW-846, and updating methods 8081, 8082 and 8270 to include new extraction techniques. Laboratories interested in obtaining a copy of the proposed Update IVA should contact the RCRA hotline at (800) 424-9346 or TDD (800) 553-7672 (hearing impaired). For information on specific aspects of Update IVA methods, contact the Methods Information Communication Exchange (MICE) Service at (703) 821-4690, or by email at mice@lan828.ehsg.saic.com.



DRINKING WATER

EPA incorporates revised analytical methods for regulated drinking water contaminants

Direct Final Rule, Federal Register, Sept. 3, 1998

The U.S. Environmental Protection Agency published a direct final rule in the September 3, 1998 Federal Register that implements new versions of currently approved EPA, American Society for Testing and Materials (ASTM), and *Standard Methods for the Examination of Water and Wastewater* (Standard Methods) procedures for compliance with drinking water standards and monitoring requirements. Compared to the currently approved versions, the new methods contain primarily editorial or technical changes that make the methods easier and safer to conduct. The rule also withdraws previously approved versions of EPA methods. Previously approved versions of ASTM and Standard Methods are not withdrawn. In this action, EPA is recommending additional methods for monitoring of chloride and sulfate which are regulated under the National Secondary Drinking Water Regulations. In addition, EPA is proposing minor technical corrections and clarifications to the regulations, including changing the composition of proficiency testing samples and requiring successful analysis of these samples once each year.

EPA is promulgating these methods as a direct final rule because the agency does not expect negative comments and wants to ensure prompt availability of the methods for compliance monitoring. This final rule will become effective without further notice on January 4, 1999, unless EPA receives ad-

(Please see Federal Update on page 7)

(*Federal Update*, from page 6)

verse comment by November 2, 1998. The rule is available for public review and downloading on the internet at <http://www.epa.gov/fedrgstr>. Copies of final methods published by EPA are available for a nominal cost through the National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161. NTIS also may be reached at (800) 553-6847. All other methods must be obtained from the publisher. For more information, contact the EPA Safe Drinking Water hotline at (800) 426-4791.

EPA releases revised analytical methods for pesticides and microbial contaminants in drinking water

Proposed Rule, Federal Register, July 31, 1998

EPA proposed the use of a new membrane filter medium for the detection of total coliform and new analytical methods for compliance determinations of acid herbicides (515.3) and diquat (549.2) in drinking water in the July 31, 1998 *Federal Register*. In this rule, EPA proposed withdrawing approval of the previous version of the EPA method for diquat (549.1) but is not withdrawing methods 515.1 and 515.2 for the acid herbicides. EPA is also proposing to amendments to clarify laboratory certification requirements. The comment period for this rule closed on September 29, 1998. For more information, contact the EPA Safe Drinking Water hotline at (800) 426-4791.

**Wisconsin Laboratory Certification and
Registration Program Information
(608) 267-7633**

WASTEWATER

EPA incorporates method 1631 for the measurement of mercury

Proposed Rule, Federal Register, May 26, 1998

In the May 26, 1998 *Federal Register*, EPA proposed amending the guidelines establishing test procedures for the analysis of mercury under the Clean Water Act in 40 CFR Part 136. This proposed rule will add method 1631: *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence*. EPA method 1631 was developed to improve the reliability of mercury measurements at the levels associated with ambient water quality criteria. EPA has promulgated water quality criteria for mercury at 12 parts-per-trillion (ppt) in the National Toxics Rule, and published guidance criteria for mercury at 1.8 ppt in the Water Quality Guidance for the Great Lakes System. EPA method 1631 must be used in conjunction with clean sampling and laboratory techniques to preclude contamination at the low levels necessary for mercury determinations. This rule also announces that EPA has developed guidance documents on sampling and clean rooms for trace metals, including mercury. The comment period for this rule closed on July 27, 1998. Method 1631 is available for downloading on the internet on EPA's home page at <http://www.epa.gov/OST>. The Wisconsin laboratory certification program has been certifying laboratories for low-level mercury analysis using this procedure for over one year. Laboratories recognized by the Wisconsin certification program are listed on page 8. If you would like to find out more about low-level mercury testing in Wisconsin, please contact Donalea Dinsmore at (608) 266-8948 or by email at dinsmd@dnr.state.wi.us.

(Please see *Federal Update* on page 8)

Laboratories accepted for low-level mercury in Wisconsin

Lab Name	State	Phone	Methods	Reagent H ₂ O MDL (ng/L)	Matrix MDL (ng/L)
Battelle Marine Sciences	WA	(360) 683-4151	1631	0.11	0.115
Brooks-Rand, Ltd.	WA	(206) 632-6206	1631	0.2	0.2
Frontier Geoscience	WA	(206) 622-6960	1631	0.27	0.78
Green Bay Met. Sewerage Dist..	WI	(920) 432-4893	245.1	8.0	10.0
Madison Met. Sewerage District	WI	(608) 222-1201	245.1 & P&T	5.5	9.0
Northern Lake Services	WI	(715) 478-2777	245.7 & 1631	6.2	9.7
S-F Analytical Laboratories	WI	(414) 475-6700	245.1	16.1	19.4
WI State Laboratory of Hygiene	WI	(800) 442-4618	1631	0.14	6.0

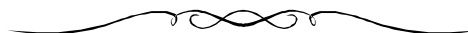
“Available cyanide” method proposed

Proposed Rule, Federal Register, July 7, 1998.

EPA has proposed adding a method for available cyanide to the list of approved procedures for wastewater analyses in the July 7, 1998 Federal Register. This procedure is being proposed as an alternative to cyanide amenable to chlorination. Both of these methods attempt to measure cyanide species that dissociate in the presence of chlorine or acid. EPA is looking for an alternate method because the cyanide amenable to chlorination test is highly susceptible to interferences from substances other than cyanide that can react in the chlorination process. The new method (OIA-1677) uses innovative technology, combining ligand exchange, flow injection analysis, and amperometry to improve detectability. This procedure is fast and is nearly immune to interferences that artificially inflate results. Preliminary data suggest that the ligand procedure almost always yields lower results than the cyanide amenable to chlorination procedure.

The preamble to the rule discusses the relative merits of the procedure, including

greater specificity for cyanide in matrices where interferences have been encountered, improved precision and accuracy compared to approved cyanide amenable to chlorination methods, lower detection limits for available cyanide, improved analyst safety, shorter analysis time, and reduced laboratory waste. One drawback of the new procedure is that method OIA-1677 does not perform as well for samples that contain high concentrations of nickel, mercury or silver cyanide complexes. EPA is recommending that cyanide amenable to chlorination remain the appropriate method for discharges known to contain these cyanide complexes in high concentrations. The comment period on this rule closed on September 8, 1998. When approved, it is likely that the DNR will begin using this procedure for permit application and permit compliance monitoring. For more information on Wisconsin's plans to implement this procedure, contact Donalea Dinsmore at (608) 266-8948 or by email at dinsmd@dnr.state.wi.us.





DNR accepting nominations for the lab of the year

Jeffrey Ripp, Laboratory Certification Program

The Wisconsin Department of Natural Resources annually recognizes two registered laboratories for their outstanding commitment to producing high quality data. The awards are presented at the Natural Resources Board meeting in March of each year. DNR presented the 1998 awards to Dairyland Power Cooperative's environmental laboratory in LaCrosse and the City of DePere's wastewater treatment plant laboratory. Last year, DNR received nominations for a number of worthy facilities. As always, choosing the two recipients was difficult. The laboratory certification and registration program looks forward to receiving another pool of qualified candidates for 1999.

The Wisconsin Department of Natural Resources is accepting nominations for the 1999 awards until December 31, 1998. Laboratories may be eligible for one of two award categories; one for smaller facilities and one for larger facilities. Small facilities generally test a small number of samples each year and are registered only in categories 1 through 4. Larger laboratories are registered in more test categories than just 1 through 4 or analyze a large number of samples each year. Nominations are open to DNR staff and to the public, but a laboratory may not nominate itself for the award. The winners will be selected by a committee in January. Nominees for the award must meet the following criteria:

- The lab must be a Wisconsin registered laboratory in good standing, with no outstanding enforcement actions. Certified laboratories will not be considered.
- Nominees must be located in the State of Wisconsin.

- Nomination forms must be received by December 31, 1998.

To nominate a Wisconsin registered laboratory for the 1999 Lab of the Year award, simply complete a nomination form and attach a brief summary no more than three pages long of why you think the laboratory deserves the award. Be sure that you can clearly justify, with specific examples, which of the criteria listed on the form you feel that the nominee meets. Nomination forms are available from Jeff Ripp at (608) 267-0579, or by email at rippj@dnr.state.wi.us. Please return completed forms no later than December 31, 1998 to the Wisconsin Department of Natural Resources, c/o John R. Sullivan- SS/6, 101 S. Webster St., P.O. Box 7921, Madison, WI 53707-7921 or by FAX at (608) 266-5226.

Changes to NR 149 effective July 1, 1998

Revisions to chapter NR 149, Wis. Adm. Code, pertaining to laboratory certification and registration were published in the June 15, 1998 Wisconsin Administrative Register. These changes became effective on July 1, 1998. This rule was revised in 1998 to add test procedures, clarify the application and renewal processes and make general corrections. Included in this rule are new tests for glycols, explosive residues and sulfate in drinking water. The Department is now accepting applications for certification for these tests. Any laboratory interested in applying should obtain a current copy of the application form (form 4800-002) from the DNR's web site or by calling (608) 267-7633. Copies of the revised rule are included in the new "Yellow Book" package mailed to laboratories earlier this fall.

Is your laboratory year 2000 compliant?

John R. Sullivan, Chief of Analytical and Statistical Services

Laboratories need to be aware of possible problems that may occur with data management software and analytical instrumentation, that is not year 2000 compliant. Most laboratories have critical business functions and systems that could experience problems, such as billings and their laboratory information system. As your partner in the laboratory business we urge you to treat the year 2000 issue as a priority among your information technology issues.

This may become a compliance issue, because the Wisconsin laboratory certification and registration program expects that your data retrieval systems continue to operate past the year 2000. Chapter NR 149, Wis. Adm. Code, requires that laboratory records be available for review for three years from the date of analysis. This applies to both electronic and hand-written records. If a laboratory is unable to access requested records, the lab will be considered in non-compliance with the code. All labs are advised to investigate the year 2000 compliance status of their electronic data storage and retrieval systems, and work with the vendors providing the software to ensure that a potentially catastrophic situation is avoided. If you have questions or concerns about the year 2000 issue, please contact Greg Pils at (608) 267-9564 or by email at pilsg@dnr.state.wi.us.



Requirements for applications for hexane extractable material

Greg Pils, Wisconsin Audit Chemist

Laboratories wishing to become certified or registered to perform Hexane Extractable Materials (HEM) testing by EPA method 1664 are reminded that they must include the following materials in their application package:

- (1) A completed application form. Past versions of the application for laboratory certification and registration (form 4800-002) did not include HEM as an option under test category 4. The most recent (June 1998) revision does.
- (2) A valid method detection limit study verifying that the laboratory has achieved an MDL of ≤ 1.4 mg/L for HEM and/or ≤ 1.6 mg/L for Silica Gel Treated HEM (SGT-HEM)
- (3) An acceptable initial precision and recovery study using four replicate spikes of the precision and recovery standard described in method 1664. The average percent recovery of the four replicates must be 83-101% for HEM and 83-116% for SGT-HEM, while standard deviations must be $\leq 10\%$ for HEM and $\leq 13\%$ for SGT-HEM.

Of course, a check covering the application and category fees is also required. Laboratories currently certified to perform oil and grease testing by freon extraction are not automatically certified to perform HEM testing, and must submit an application if they wish to pursue certification for this test. The two tests will appear separately as "Oil and Grease (Freon)" and "Oil and Grease (HEM)" on certificates. For more information regarding HEM certification, contact Greg Pils at (608)267-9564 or email at pilsg@dnr.state.wi.us.

COUNCIL CORNER

Dave Kollakowsky, Council Member

My fees keep going up, I keep getting new auditors, and then there's this NELIFT - or is it NELAC? - thing. What's up with that? If you have questions or concerns about the Wisconsin laboratory certification and registration program that maybe you would prefer not to discuss with the program's staff, consider contacting your Certification Standards Review Council representative.

The Council needs your input to help guide discussions and decisions concerning the Wisconsin laboratory certification and registration program. Without your feedback, we are left to oversee the program based on our best judgment, and the views of the minority which choose to contribute. We believe that many of you have a "hot button" or issue with some aspect of the program and we would like to hear about it. A portion of each quarterly meeting is devoted to issues brought forward by Council members. This is an opportunity for Council members to raise your particular issues and concerns for discussion. Beyond that, if you are passionate enough about a particular issue or have an interest in what is going on at the Council meetings, feel free to come. All Council meetings are open to the public. Meeting dates are posted on the DNR's web site. Meeting agendas are finalized about a week before each meeting and are available from the laboratory certification and registration program.

If you don't feel like coming to the meetings, you can still find out what issues are being discussed by looking at the meeting minutes. The minutes are available on the laboratory certification program's web site. The Certification Standards Review Council encourages you to talk to your representative. We would like to hear from you.

Dave Kollakowsky was appointed to the Council in 1996 and represents industrial laboratories.

The Certification Standards Review Council is a nine member citizen advisory body to the DNR laboratory certification and registration program. Its members represent diverse interests in the environmental field and are appointed by the Wisconsin Department of Administration to three year terms.

1998 Council Members

Commercial Laboratory

Ms. Mary Christie, Chair
En Chem, Inc.
205 Seagull Drive
Mosinee, WI 54455
(715) 693-1953

Public Water Utility

Ms. Ruth Klee Marx
Marathon Co. Health Dept.
1200 Lake View Drive
Wausau, WI 54403-6797
(715) 842-7891 ext. 337

State Laboratory of Hygiene

Dr. Bill Sonzogni
State Lab of Hygiene
465 Henry Mall
Madison, WI 53706
(608) 262-8062

Large Municipal Wastewater Plant

Ms. Debbie Cawley
Green Bay MSD
2231 N. Quincy St.
Green Bay, WI 54307
(920) 432-4893

Agricultural Interest

Mr. Bill Bruins
Self Employed Farmer
(920) 346-5293

Small Municipal Wastewater Plant

Mr. Gilbert Williams
Vice Chair
Sun Prairie WPCF
300 East Main
Sun Prairie, WI 53590
(608) 837-6292

Industrial Laboratory

Mr. David Kollakowsky
WEPCO
PO Box 2046
Milwaukee, WI 53201
(414) 221-2835

Solid and Hazardous Waste Disposal Facility

Ms. Barbara Hill
Waste Management
2100 Cleanwater Drive
Geneva, IL 60134
(630) 208-3100 ext. 112

Interest in Laboratory Certification

Mr. Russell Janeshek
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Green Bay, WI 54307
(414) 497-2500

Council Information on the Web

www.dnr.state.wi.us/org/es/science/lc/council



DNR implements dissolved-based effluent limitations

New limitations require “clean” sampling and analysis

Donalea Dinsmore, DNR QA Coordinator

As part of the Great Lakes Initiative, DNR revised chapter NR 106, Wis. Adm. Code, which contains rules for regulating toxic chemicals. Provisions in this code allow permittees to request dissolved-based effluent limits that are somewhat higher than limits based on total recoverable metals. The DNR expects that this provision will be most often applied to metals limits for dischargers in the northwestern part of the state, an area with soft water. Because metals toxicity is a function of water hardness, areas with soft water have lower acute and chronic toxicity criteria for most metals.

Calculating dissolved-based limits involves estimating the assimilation capacity of the receiving water using a site-specific “translator”. To derive the translator for a metal, the limits calculator needs, among other things, the concentration of both total recoverable and dissolved metals, hardness, and suspended solids in the river or stream. To reduce uncertainty, the analytical procedure must be sensitive enough that all measurements fall well into the region of quantitation. Measurements showing non-detects are unusable for the translator calculation.

The Department has most frequently applied the dissolved-based limit approach for copper, so this metal provides a good example. Copper is a problem because it is both ubiquitous and more toxic to aquatic life than it is to humans. Existing low-level data from Wisconsin ambient stream samples indicate levels of copper ranging from a low of about 0.1 µg/L up to around 10 µg/L, with most of the data falling between 0.5 and 3

µg/L. To obtain quantifiable results for stream concentrations in the 0.5 µg/L range, the detection limit for copper needs to be around 0.1 µg/L. When the stream concentration is in the 0.1 µg/L range, detection limits need to be around 0.02 µg/L. Obtaining detection limits at these levels requires clean sampling and analytical techniques. Unfortunately, the Department does not have enough data to reliably predict when the more sensitive detection limits are needed. The same level of sensitivity is not necessary for effluents because the lowest effluent limitation is around 5 µg/L. Nevertheless, the Department is concerned that effluent data may be biased by contaminants in the sampling and analytical process.

Sampling is the first and arguably the most important step in generating reliable environmental data. Experience has shown that careful sampling and analysis using clean techniques is required to avoid sample contamination, which makes results unreliable for ambient samples. As dissolved-based limits are implemented, DNR staff will perform ambient water sampling and have the analyses done in the clean room at the State Laboratory of Hygiene. Once the DNR establishes a broad database on ambient metals concentrations, the Department will be in a better position to refine the data quality objectives and transfer the technology to the commercial sector. If you would like more information, please contact Donalea Dinsmore at (608) 266-8948 or by email at dinsmd@dnr.state.wi.us.

EPA SAFE DRINKING WATER METHOD HOTLINE

Did you know that questions regarding EPA’s drinking water methods can be submitted via email to: DWMMethods.Help@epamail.epa.gov?

DNR investigates detection limits; will release report

Kerilynn Carden and Jeffrey Ripp, Laboratory Certification Program

Since 1990, the Wisconsin Department of Natural Resources has published several rules requiring laboratories to report analytical data down to their established limits of detection (chapters NR 149, 105 and 809, Wis. Adm. Code). Last spring, the DNR requested that certified and registered laboratories submit method detection limit (MDL) information for a number of analytes. The questions that many laboratories and regulated facilities have been wondering are: why is the DNR so concerned about data at these low levels and why has the laboratory certification and registration program focused on EPA's method detection limit procedure? The answer to the first question is simple. The earliest possible detection of toxic or potentially carcinogenic chemicals in the environment is paramount in the DNR's mission to protect human health, wildlife, fish, and the environment. Low level data is important information needed by agency decision makers. In cases where health-based standards fall below typical laboratory detection limits, low level data are critical for making the correct choices when designing site remediation strategies, alerting the public to health threats, and protecting wildlife from toxic chemicals.

Answering the second question is more difficult. The DNR has based its low level data reporting strategy on the EPA's MDL procedure, found at 40 CFR Part 136, Appendix B. Despite criticisms of the statistical validity of this procedure, the DNR continues to rely on this method for a couple of reasons. First, the procedure is widely distributed across the United States. Because the procedure is required nationwide for many certification programs, regulatory agencies can accept data from laboratories in virtually any state as long as the laboratory calculated its detection limits using the MDL

procedure. The data are "portable", and data users know how to interpret low level detects and compare results generated by different labs. Second, whether you love it or hate it, the procedure is simple to understand and easy to perform in the laboratory. The MDL procedure can be used to determine detection limits across a wide variety of instruments, detectors and methods. In comparison to some other options for calculating detection limits, the MDL procedure is cheap. Of course, because the procedure is generic, data users need to be educated about what environmental data actually mean when results fall near the detection limit.

Data users that know how to properly interpret low level environmental data understand analytical variability near the detection limit. This variability occurs both within and across laboratories. As the DNR began implementing new low level reporting rules, the laboratory certification program realized the need to determine the range of capabilities across Wisconsin certified and registered laboratories. The result was the spring 1998 survey of detection limit capabilities. The primary purpose of this survey was to gather information on the range and variability of MDLs calculated by Wisconsin certified and registered laboratories for a select list of compounds of special concern. These compounds were selected based upon the magnitude of their health-based standards and the DNR's perception of analytical capabilities in the laboratory industry. The DNR is reviewing the submitted MDL information to determine if one type of instrument or method consistently produces lower MDL results.

Another survey objective was to determine the percentile ranges of laboratories capable of achieving MDLs at different lev-

*(Please see **Detection Limits** on page 14)*

els. The DNR is evaluating the detection limit information against the health-based standards to see if labs can routinely detect compounds at those levels. For each compound, the DNR is preparing a summary of the levels where 75, 50 and 25 percent of the labs can routinely detect a chemical. Based on this information, DNR permit drafters and field staff will be better equipped to decide whether or not a laboratory's results are sufficiently low enough in cases where low level information is required.

The Department is preparing a report which will include summary statistics, percentiles, and other useful information about MDLs calculated by Wisconsin certified and registered laboratories. Because the intent of this project was to get an overview of laboratory capabilities, individual laboratories will not be identified in the final report. Each laboratory that participated in the survey will receive a customized report that shows how their results compare with the other participants. The final report will be released in late 1998 and will be available for free on the internet. Paper copies of the report will be mailed to public research libraries and will be available from the Wisconsin Department of Administration's Document Sales. For information about the report, please contact Kerilynn Carden at (608) 266-9255 or by email at cardek@dnr.state.wi.us.



Understanding the MDL procedure

Even though the EPA's method detection limit (MDL) procedure is straightforward, the number of laboratories that submit improperly calculated MDLs is surprising. Out of 119 laboratories that submitted data for the 1998 MDL survey, only 17% of the laboratories submitted correctly calculated MDLs for every chemical. The remaining 83% had at least one problem with their MDL determinations. A quarter of the submitted results had to be removed from the data set because they did not meet one or more of requirements of the MDL procedure.

Twenty-five percent of all MDLs were calculated incorrectly! Take some time to think about the previous sentence. This percentage is clearly much higher than should be expected for a procedure that has been around as long and is as widely used as the MDL procedure. The DNR has identified four major problems that appeared regularly in the MDL survey data. It would be useful for laboratories to review their MDLs to make sure that none of these problems exist. During an on-site evaluation, Wisconsin's auditors will review your MDL data, and could cite your laboratory for a deficiency if any of these problems are found.

Problem #1: Spiking too high or too low. The MDL procedure requires the concentration of each replicate to be greater than the calculated MDL, but less than ten times the calculated MDL. Be sure to review each result to make sure that it falls within the appropriate concentration range.

Problem #2: Miscalculating the MDL. This error can result from a variety of factors, including using the wrong Student's t-value, using the population standard deviation instead of the sample standard deviation, reporting the wrong units, or simply making

a mathematical error. Always double check your calculations.

Problem #3: Using an insufficient number of replicates. This is the simplest error to avoid. The MDL requires that you use at least 7 replicates. If you feel that you need the insurance because you may wish to later discard one replicate as an outlier, use 8 replicates.

Problem #4: Not enough supporting information. Because the MDL is method and instrument specific, it is important to retain all of the information associated with a calculated value, including which instrument the MDL was determined on, what method was used, when the MDL was calculated, etc. The DNR survey asked for quite a bit of supporting information. In some cases, laboratories neglected to submit everything that was desired.

Linear dynamic range determination required for metals analysis

Greg Pils, Wisconsin Audit Chemist

Failure to determine an instrument's linear dynamic range (LDR) is a commonly cited deficiency for metals. EPA's *Methods for the Determination of Metals in the Environment* (EPA/600/4-91/101 and EPA/600/R-94/111) as well as SW-846 method 6010B, require the analyst to determine an instrument's linear dynamic range for each metal and absorption or emission wavelength used to report analytical results prior to using the instrument for analysis.

The procedures for determining the linear dynamic range differ slightly from method to method and can be difficult to interpret correctly. Adherence to the following guidelines should insure compliance with this often confusing method requirement:

1. Establish a valid linear calibration curve. This curve should be generated using the same calibration standard concentrations used for sample analysis and quantitation.
2. Analyze solutions of progressively higher known concentrations until one yields a result of greater than 10% below the true value (i.e., $\leq 89\%$ recovery). The largest known concentration of analyte that can still yield an observed concentration of less than 10% below the true value (i.e., $\geq 90\%$ recovery) is equal to the instrument's linear dynamic range. At least six known concentrations must be analyzed. These may include the standards used to generate the calibration curve. For example, if the calibration curve was constructed using a blank and three standards, at least three more solutions of known concentration must be analyzed for the linear dynamic range determination to be considered valid.
3. Once a valid linear dynamic range has been established, any sample determined to possess a concentration of analyte greater than 90% of the instrument's linear dynamic range for that element must be diluted and reanalyzed.

Linear dynamic ranges must be kept on file, and should be verified annually or whenever there has been a significant change in the operating conditions of the instrument. If you have any questions about linear dynamic range requirements for metals analysis, please contact Greg Pils at (608) 267-9564 or by email at pilsg@dnr.state.wi.us.



The Auditor's Corner

Alfredo Sotomayor, Senior Audit Chemist

My "Everything": Record & Data Audits

During on-site evaluations, most auditors will perform a record and data audit, which involves selecting samples and following them through a document trail. This method allows auditors to directly assess a laboratory's record keeping practices, and indirectly, but quite effectively, assess whether a laboratory adheres to method requirements, to its quality assurance manual, and to good laboratory practices. When I confirm an appointment for an evaluation, I inform my contact that I intend to conduct a data review audit as part of the on-site evaluation. I often say "I want to see *everything* regarding and affecting the samples I select for tracking." At the laboratory, I repeat the statement, and give examples of the documents I need to examine. I have to admit that my idea of "everything" does not always match with the laboratory's quality assurance officer. This is not usually the quality assurance officer's fault; different auditors have different ideas of what they need and want to see during a data review audit.

In this column I will give you my list of essentials and some tips on how to make the data review portion of an audit proceed smoothly. You can safely assume that other auditors from Wisconsin will have similar expectations. Tips first, lists later.

BEFORE THE ON-SITE VISIT

Chapter NR 149, Wis. Adm. Code, requires laboratories to maintain records of processed samples for three years unless the Department has specifically requested a longer period for samples involved in legal action. You should make sure that your lab can retrieve any pertinent records for that period. If you store records off-site, this does not mean you will have to transport all rec-

ords within the three year period back to the laboratory; all you need to do is to provide the auditor with the records of the selected samples while he or she is on-site. The number of samples selected will vary depending on the size and the certification scope of a laboratory. Being able to retrieve the pertinent records while the auditor is on-site is a good indicator of the efficiency of your record-keeping system.

Selecting sample numbers for tracking often consumes some time during the audit because not all samples are analyzed for compliance with covered DNR programs. This is particularly true at out-of-state laboratories. I have started to request lists of sample identification numbers and tests performed for Wisconsin regulatory samples before my visits. This enables me to make informed selections and gives the laboratory time to start to retrieve records early during the visit, while other parts of the audit take place. If your laboratory does not have an easy way of determining which samples analyzed are covered under the Wisconsin laboratory certification and registration program, I urge you to start developing this capability.

DURING THE ON-SITE VISIT

I always appreciate having a quiet area with a long table, where I may be able to conduct interviews with analysts and spread out documents for review. I often request that an informed member of the laboratory staff, typically the quality assurance officer, remain with me while I am reviewing records. Although this ties up laboratory personnel for an extended time, it is beneficial to me and the laboratory. I do this for several reasons. Different laboratories keep documents in different formats and having someone there to explain the laboratory's system speeds up the review. Having a laboratory representative at hand during the data review also allows me to give immediate feedback and can help clarify misconceptions or incor-

rect conclusions that I may make during my review before they are mentioned at the exit interview or in the audit report. If I were on the other side, I know that I would like to be around any auditor reviewing laboratory sample records.

THE "A LIST"

The "A" list includes documentation that I will certainly request to see during an on-site evaluation. This list is really the documented version of that familiar game, "I am a sample; take me through your laboratory." This game is usually played with a client or plant sample, but can be played as well using a proficiency testing sample. In this column I cannot give an extensive description of what each document should contain, but I have given brief explanations for some items, where warranted.

1. *Field documents* - If the laboratory is responsible for sampling, documents pertaining to sample collection and tests performed in the field will need to be reviewed.
2. *Sample receipt documents* - These should indicate the date and time of arrival, and the preservation status on receipt. Chain of custody reports, if required, may also contain this information.
3. *Analytical process records* - These should document absolutely every preparatory and analytical procedure that a sample being tracked has undergone. Here are some examples:
 - Digestion records
 - Distillation records
 - Extraction records
 - Moisture determination records for applicable solid samples
4. *Instrument records* - These may have been generated before or on the day that the sample being tracked was analyzed.
5. *Initial calibration records*
6. *Continuing calibration records* - If a full calibration is not performed on the day of analysis, the initial calibration being verified must be referenced in the continuing calibration records.
7. *Instrument diagnostic records* - Examples are mass spectrometer tune verifications, column degradation checks and plasma optimization checks.
8. *Sequence logs* - These should show the sample number in the analytical queue and must document that the sample was analyzed within holding time and bracketed by the appropriate quality control samples.
9. *Sample analysis records* - These contain the raw data associated with the sample. They can be instrument outputs or manual notations, but they must contain the raw data that was used by an instrument or analyst to arrive at the concentration of analytes reported for the sample and need to be correlated to the initial calibration event.
10. *Quality control documents* - These document the analysis of quality control samples as well as qualifiers about the samples being tracked.
11. *Blanks*
12. *Laboratory fortified blanks* or laboratory control samples
13. *Matrix spikes* or laboratory fortified matrix, and matrix spike duplicates or replicates
14. *Second source quality control checks*, when applicable
15. *Quality control limits* - The limits of interest are those in place at the time that the samples were analyzed. Depending on the type of quality control sample assessed, these limits can be fixed or statistically-derived, but they should all be posted and available to the analysts.
16. *Corrective action records* - These demonstrate investigations and actions taken to address quality control failures. These generally affect more than just the sample being tracked.
17. *Final report* - A copy of the report sent to the client and any documents ad-

addressing QC failures or anomalies associated with the analyses, including flags accompanying results.

THE "B LIST"

This list relates to the capabilities and quality assurance processes that I expect to be documented at a laboratory. An auditor may not request of all this information during the data review exercise. In many cases, the auditor may have examined the records on the "B" list during a detailed tour of the laboratory or prior to the on-site visit. Nevertheless, this information should be available on demand. I request these during the data review exercise when I have found problems and need more information.

1. Documents tracking the provenance and disposition of all stocks used for analytical standards, and reagents used in analyses.
2. Instrument maintenance logs
3. Initial demonstrations of competence or performance for all analysts.
4. MDL studies for all applicable analytes reported by the laboratory.
5. Quality checks on reagent water

6. Calibration verification for analytical balances, automatic pipettes, thermometers, and other equipment measuring physical properties.
7. Documents summarizing the data used to generate in-house quality control limits.

PAPER OR PLASTIC?

Any of these documents can be provided electronically if that is the only way in which records are maintained by a laboratory and transmitted to a client. If paper copies are also maintained, then electronic versions are satisfactory as long as a laboratory is able to demonstrate that the electronic copy is a faithful representation of the hard copy. Of course, all electronic records must be safeguarded from alteration and corruption. For laboratories relying heavily on electronic archives, it is not unusual for an auditor to request retrieval from magnetic media to test this type of documentation. I do this frequently with GC/MS data.

When I cannot complete the document review during an on-site visit I either request that the documents be copied and sent to my office or I schedule a revisit to complete the process.

New laboratory certificates mailed

After a long summer wait, the new certificates for Wisconsin certified and registered labs are all out the door! Because of computer delays, most of the certificates were printed and mailed during the last week of August instead of the planned June and July printing. If your laboratory does not yet have a new certificate, please contact the laboratory certification program at (608) 276-7633. The new certificates expire on August 31, 1999 and may look slightly different than your previous certificate. Drinking water certified labs may notice that for the first time, they did not receive two separate certificates for their drinking water and non-drinking water certifications. All of a laboratory's certifications now appear on a single certificate. The only time a lab will receive a two page certificate is when there is not enough room for all of a laboratory's certifications on one page.

Required certification for hazardous waste characterization

Diane Drinkman, Wisconsin Audit Chemist

A laboratory that is not certified for ignitability receives a sample that looks and smells like a mixture of organic solvents. The chain of custody sheet states that the client wants a flash point determination on the sample. The laboratory takes the Pensky-Martens closed cup tester down off the shelf and determines that the mixture flashes at 115 degrees Fahrenheit. Based on this information, the client properly disposes of the material as a flammable liquid, with a hazardous waste code of D001. In this scenario, the laboratory is required to be certified by the Wisconsin program for ignitability in category 7 in order to do a flash point. The test "flash point" doesn't appear on the certificate, and the client (or generator to follow hazardous waste nomenclature) certainly may not realize that they are violating the hazardous waste codes by having their waste characterized by an uncertified lab.

In recent months, auditors have discovered that some laboratories have been performing hazardous waste characterizations without the proper certification. The following paragraphs will help to clear up some of the confusion about hazardous waste characterization by describing how these determinations fit into the Wisconsin certification program.

A solid waste is defined as a hazardous waste if it:

- ✱ Exhibits a characteristic of a hazardous waste (D-list),
- ✱ Is a hazardous waste from a nonspecific source (F-list),
- ✱ Is a hazardous waste from a specific source (K-list),
- ✱ Has been found to be acutely toxic (P-list), or

- ✱ Is a toxic commercial chemical product or manufacturing intermediate (U-list).

Tables II-IV in chapter NR 605, Wis. Adm. Code, identify those constituents on the F, K, P and U-lists. It is the D list that presents the most confusion. The characteristics of hazardous wastes are further defined in s. NR 605.08, Wis. Adm. Code, as *ignitable*, *corrosive*, *reactive* or *toxic*.

Ignitability is defined as a liquid, other than an aqueous solution containing less than 24% alcohol by volume, having a flash point less than 140° F; is not a liquid and is capable, at 25° C and pressure of one atmosphere of causing fire through friction, absorption of moisture or spontaneous chemical changes and, when ignited, burns vigorously enough to create a hazard; is an ignitable compressed gas; or is a chemical oxidizer. Laboratories can determine if a liquid is ignitable by using a Pensky-Martens or Setaflash closed cup tester following approved procedures. The sample generator will typically be interested if the material flashes below 140° F after which the generator will assign the waste with hazardous waste code D001. If a laboratory is testing the flash point of a material to determine if it meets the characteristic of ignitability, then the laboratory must be certified for ignitability in category 7.

Corrosivity is defined as an aqueous solution with $\text{pH} \leq 2$ or ≥ 12 as determined by a pH meter following approved methods, or if it is a liquid and corrodes plain carbon steel with a carbon content of 0.20% at a rate > 6.35 mm per year at 55° C, following approved methods. The characteristic of corrosivity can be determined by a laboratory by either performing the metal "stamp" test or by determining sample pH. A $\text{pH} \leq 2$ or ≥ 12 will require assigning hazardous waste

(Please see **Hazardous Waste** on page 20)

code D002. Laboratories need to be certified for corrosivity in category 7 to determine this characteristic.

Reactivity is the most complex of the characteristics. A waste is defined as “reactive” and assigned hazardous waste code D003 if it is normally unstable and readily undergoes violent change without detonating, reacts violently with water, forms potentially explosive mixtures with water, generates toxic gases, vapors or fumes when mixed with water, is a cyanide or sulfide-bearing waste, capable of detonation or explosive reaction, or a forbidden explosive. If a laboratory is analyzing a material to determine if it meets the characteristic of reactivity, then the laboratory must be certified for reactivity in category 7. In addition, the laboratory must be certified for cyanide and sulfide analysis under category 6.

The characteristic of **toxicity** has evolved since first identified by U.S. EPA in the 1980's. The Toxicity Characteristic Leaching Procedure (TCLP) is used as a preparatory step to determine if a waste material contains one, or more compounds assigned hazardous waste codes D004-D043. This list includes metals, volatile organic compounds, pesticides and semivolatile compounds. A laboratory determining if a material meets the definition of the characteristic of toxicity must be certified for TCLP in category 7, as well as the determinative step, i.e., metals in category 8, VOCs in category 10, pesticides in category 14 or 16, and semivolatiles in category 11 or 12.

If your laboratory is performing analyses for hazardous waste determinations, make sure that you are certified to perform the appropriate tests. If you are not presently certified for ignitability, corrosivity, reactivity or TCLP and wish to perform these analyses, you will need to submit an application to the Wisconsin laboratory certification program. Remember that laboratories performing analysis without proper certification run the

risk of being referred to the Wisconsin Department of Justice for prosecution. Companies or individuals that have waste determinations carried out by uncertified laboratories are also at risk of enforcement for violation of the hazardous waste codes. For more information about hazardous waste characterization issues, please contact Diane Drinkman at (608) 264-8950 or by email at drinkd@dnr.state.wi.us.

ASTM Method D-93-96 for Flash Point

Subdivision 605.08 (2)(a)1, Wis. Adm. Code, was revised in the May 1998 Wisconsin Administrative Register to replace the reference to method ASTM D-93-85 with ASTM D-93-96 for the determination of flash point. The new citation (ASTM D-93-96) has quality control limits of $\pm 1^\circ \text{F}$ for 1,4-dimethylbenzene compared to $\pm 2^\circ \text{F}$ in the previous method. A number of laboratories have commented that this quality control limit in ASTM D-93-96 is too tight, and simply cannot be routinely achieved. More recent revisions to this standard (ASTM D-93-97) have more flexible quality control limits. The currently federal regulations (40 CFR 261.21) cite ASTM D-93-79 or ASTM D-93-80.

Laboratories certified under chapter NR 149, Wis. Adm. Code, should use ASTM D-93-96, with the tighter QC limits, until subd. 605.08 (2)(a)1, Wis. Adm. Code, can be revised or the Bureau of Waste Management issues a variance from this requirement. Contact Dave Parsons in the Bureau of Waste Management at (608) 266-0272 for more information.

WASTEWATER LAB FORUM

Rick Mealy, Wisconsin Audit Chemist

Ed. Note: The “Wastewater Lab Forum” is a new section of *LabNotes* geared towards municipal and industrial laboratories. Articles in this section will cover issues related primarily to basic water quality tests performed on wastewater effluents. Let us know what you think about this new section. Ideas and comments for future Wastewater Lab Forums are welcome. Send comments to Jeffrey Ripp, *LabNotes* Editor, 101 S. Webster St., Box 7921, Madison, WI, 53707 or by email at rippj@dnr.state.wi.us.

Phosphorus calibrations: finding the real “best” fit

How are you calibrating your phosphorus test? Most laboratories use a calibration curve constructed manually by plotting the concentration of phosphorus on the x-axis and absorbance on the y-axis. A straight line which best fits the data points is then drawn, and sample concentrations are determined using the “best fit” line to convert absorbance into concentration.

The laboratory certification and registration program discourages this practice because there is significant variability in both how the scale of the graph is constructed, and how any individual draws the “best fit” line through the calibration data points. This degree of variability makes it difficult to trace your results as they appear on the discharge monitoring report (DMR) back to the raw data. When a certification officer comes to your laboratory, one part of the audit process will be to verify that the absorbance for a particular sample indeed relates to the concentration reported on the DMR. In addition to the potential for the certification officer to read a different concentration from the curve, the auditor may feel that the line has not been drawn accurately (i.e., it is not the “best fit” line). Traceability of results is a critical requirement of laboratory record-keeping practices, and is described in section NR 149.06, Wis. Adm. Code.

Both sources of variability can be eliminated if a standard procedure is used to generate a calibration function. One of the most widely recognized means of achieving this is the use of a linear regression. It is likely that you will have already heard your certification officer discussing linear regressions. Linear regression equations can be generated with an inexpensive scientific calculator and most spreadsheet programs. Linear regression is a statistical procedure that will produce consistent equations for a “best-fit” line, eliminating questions about the validity of a hand-drawn line. The DNR is working to provide laboratories with more assistance in this area. Look forward to more information about this issue in future *LabNotes*.

Ammonia calibrations require three standards

Regional certification officers are still encountering a number of laboratories that are preparing ammonia calibration curves using only one or two standards. This practice has been allowed in the past because it appeared in a federal ion selective electrode method. This is no longer acceptable because this method has been deleted from both the federal regulations and chapter NR 219, Wis. Adm. Code. Currently, the laboratory certification and registration program requires the following:

NR 149.14 Quality Control. (3)(b)A calibration shall consist of at least 3 standards and a blank except as allowed in approved methods using ion selective electrodes or inductively coupled plasma.

(Please see WW Forum on page 22)

(*WW Forum*, from page 21)

All currently approved ion selective electrode methods require that calibration curves for ammonia be constructed using at least 3 standards and a blank. Many laboratories have indicated that they are using Standard Methods method 4500-NH₃ D, which actually requires the use of *five* standards. If your ion meter is not capable of using at least three standards in the calibration process, then you can construct a graph similar to that used for phosphorus, but using semi-logarithmic graph paper. The preferred alternative is to calculate a linear regression. This will result in more accurate and traceable results. Since ion selective electrodes require a logarithmic conversion, a linear regression of the log of concentration versus millivolt response is necessary. Contact your certification officer if you need assistance performing this calculation.

Permanent Records: USE INK!

Remember that all records must be maintained in a manner that “ensures their permanence”. Section NR 149.06 (5), Wis. Adm. Code, specifically requires that, “handwritten records shall be recorded in ink.” This requirement precludes the use of pencil for most laboratory records. Some of you may have already heard this from your regional certification officer. The most common records that are being made in pencil are associated with sample collection and temperature of autosamplers.

How many BOD bottles do I need to make replicates?

Laboratories have requested a clarification regarding how to prepare biological oxygen demand (BOD₅) replicates. Preparing a replicate of only a single dilution is incorrect. Replicates are required for each sample dilu-

tion used. For example, if you routinely use dilutions of 100 mL, 200 mL, and 300 mL for your effluent sample, replicate samples of the effluent should also be prepared using dilutions of 100 mL, 200 mL, and 300 mL, resulting in a total of six BOD₅ bottles.

Proper collection and preservation of VOCs in soil

Greg Pils, Wisconsin Audit Chemist

The State of Wisconsin requires all soil samples analyzed for volatile organic compounds to be preserved in methanol prior to analysis. Many of you may recall that in this past spring's edition of *LabNotes* (volume 13, number 1), I informed you that the State of Wisconsin does not recognize EPA's SW-846 method 5035 as an acceptable procedure for the collection, preservation and analysis of soil samples. Since that article was published, I have received a handful of calls asking, “Greg, just what method *will* Wisconsin accept for collection and preservation of these samples?” The answer is actually quite simple. The only method that the DNR has approved for the collection and preservation of soil samples is the *September 1995 Modified GRO: Method for Determining Gasoline Range Organics* (DNR PUBL-SW-140). All soil samples taken for volatiles analysis should be collected, preserved and extracted according to the procedures described in this document. The resulting extracts may be analyzed by any GC or GC/MS method approved for use in Wisconsin.

The GRO method is available in Adobe's PDF format on the Wisconsin laboratory certification program's web site. If you do not have internet access, or would like more information regarding the procedure, please contact me by phone at (608) 267-9564, or by email at pilsg@dnr.state.wi.us.

NELAC IV: moving towards implementation

Alfredo Sotomayor, Senior Audit Chemist

The fourth annual National Environmental Laboratory Accreditation Conference (NELAC IV) took place from June 30 to July 2 in San Antonio. Building on the momentum achieved at NELAC III, this conference focused on "fine-tuning" the standards and addressing implementation issues. As expected when moving from the potential to the actual, unforeseen and previously ignored concerns surfaced. For instance, those states that have applied to become accrediting authorities and have tailored their programs to the July 1997 version of the standards are now very concerned about effective dates for any revisions to the standards.

Officials announced at NELAC IV that the time line for granting approvals to states and for auditing laboratories has been adjusted. The first accrediting authorities are now expected to be approved by November 1998. Of the 20 applications received by the National Environmental Laboratory Accreditation Program (NELAP) from potential accrediting authorities, 10 were sufficiently complete to schedule on-site assessments. At the time of NELAC IV, assessors had only completed a partial audit of the State of Colorado. Assessors had tentatively scheduled audits for New York, New Jersey, and Illinois. Accreditation for laboratories will occur in a single block and is expected to occur by January 2000.

Participants at the conference hotly debated the content and style of the laboratory assessment checklists. Two seemingly opposite approaches were discussed: extremely detailed checklists covering every method aspect, or more general checklists that emphasize system requirements and fewer method details. With the advent of perform-

Highlights from NELAC IV

- ◆ A provision allowing the substitution of experience or a valid operators license in place of formal education for operators at wastewater treatment facilities and industrial plants was ratified. Any operator or industrial laboratory director meeting the NELAC credentials through this clause would retain the approval in perpetuity.
- ◆ The Field Measurements Committee is still ad-hoc, but is expected to become permanent at NELAC V. A straw poll taken during this conference strongly supported making this a standing committee.
- ◆ Grandfathering laboratory assessors will cease two years after the first accrediting authorities are recognized. This means that if Wisconsin were to seek NELAP recognition, all our NELAC assessors would need to pass the appropriate NELAP-approved training courses before they could audit.
- ◆ The NIST standard for proficiency testing providers was not ready at the time of the conference. This standard contains the criteria that prospective sample providers would have to meet to become NELAP approved. This means that NIST is probably a year away from granting approvals.
- ◆ References to mobile laboratories have been removed from the standards. Once the Field Measurements Committee becomes permanent, it may take on the matter of accrediting mobile laboratories.

(Please see NELAC IV on page 24)

(NELAC IV, from page 23)

ance-based measurement systems and method flexibility, many felt that detailed method checklists would become obsolete very quickly. Alfredo Sotomayor of Wisconsin participated on a committee formed by the Environmental Laboratory Advisory Board to make recommendations on these checklists. This committee favored brief, general checklists and recommended ensuring consistency of assessments through rigorous training courses for assessors.

For the first time, NELAC IV included a training course for accrediting authority assessors who will determine whether a state will be granted NELAP recognition or not. This course, while useful, is still being refined. The laboratory assessor training courses are not available yet, although their content is under discussion. A new draft of the laboratory on-site assessment training manual was distributed at the conference. You can access the manual and the latest version of the standards at the redesigned NELAP web page (see page 2). For more information about NELAC IV, please contact Alfredo Sotomayor at (608) 266-9257 or by email at sotoma@dnr.state.wi.us

Corrections to Revision 7 of the Yellow Book. Please note that the tables in Sections 5 and 6 of the new Yellow Book (DNR PUBL-TS-007-98) contain a typographical error. Tables 5.2, 5.5, 5.6, 5.7, 5.8, 5.9 and 6.2 list the units for MDLs, IDCs, PALs and MCLS as mg/L. This is incorrect. In each table, the units should be µg/L. Also, the MDL requirements for SDWA analytes have changed. Corrected sections are available on request by calling (608) 267-7633 or for free on the internet at the laboratory certification web site (see page 2).

DNR phases in new wastewater permit application

Tom Mugan, Bureau of Watershed Management

In the spring issue of *LabNotes*, the Bureau of Watershed Management reported that wastewater permit applications under the Wisconsin Pollutant Discharge Elimination System (WPDES) would change significantly. The Department is currently phasing in the redesigned permit application. Among the changes are the use of preliminary limits and a requirement to submit quality control information with all monitoring data.

The Department calculates preliminary limits for regulated dischargers and sends these limits along with the permit application. A preliminary limit represents an estimate of an effluent limitation. Preliminary limits would become actual limits only if analytical results indicate that the effluent contains high enough concentrations of the substance that the preliminary limit would be exceeded. Preliminary limits are useful for several reasons. Permittees can compare the preliminary limit for a substance to initial effluent monitoring results to determine if additional monitoring, along with less conservative statistics, might demonstrate that a limit is not necessary. Preliminary limits will also help determine what level of analytical sensitivity is required for a given pollutant at a facility. The DNR typically recommends an analytical method to use for a particular substance. The facility and its contract laboratory may choose to use a method less-sensitive than the one recommended, but permittees are not allowed to report a "no detect" for a substance using a less sensitive method unless the detection limit of the chosen method is less than one-fifth of the preliminary limit. Thus, the labo-

*(Please see **Permits** on page 25)*

(Permits from page 24)

ratory can be sure to use an appropriate method by consulting with the regulated facility regarding their preliminary limits.

Laboratories may need to change their data reporting procedures to help their clients comply with the new quality control requirement. **Labs are not being asked to generate new information.** In fact, commercial laboratory reports commonly contain much of the quality control information requested on the new application. However, as you can probably guess, the format for submittal varies considerably. The Department would like permittees to submit quality control information in a standard tabular format. The forms are mailed to permittees either as WordPerfect tables or Microsoft Excel spreadsheets. If your laboratory is able to duplicate or closely simulate one of these formats, the Department will accept the laboratory reports as attachments. Otherwise, the permittee will need to transcribe the infor-

mation from the laboratory reports on to the paper form. Copies of the spreadsheets are available from either Donalea Dinsmore, by phone at (608) 266-8948, email dinsmd@dnr.state.wi.us or from Tom Mugan by phone at (608) 266-7420, email mugant@dnr.state.wi.us. If requested, the Department will send the files electronically via email or on floppy disks.

The DNR believes that the new process will help to improve the reliability of effluent monitoring data in Wisconsin. Permittees are urged to share many parts of the application packet with their contract laboratories. The DNR hopes that laboratories stay in tune with the new process. In the future, the Department plans to implement an electronic application process. To help us in our design with the electronic application, your ideas on how the current process is working are needed. Please call either Donalea or Tom with your comments about the new permit process.

FY 1998 Billing Summary - Certified and Registered Labs

Laboratory Type	# of Labs Billed	Amount Billed	Max. Bill	Min. Bill	Average Bill
Commercial	119	\$195,375.00	\$3,787.50	\$600.00	\$1,641.81
Municipal	306	\$166,912.50	\$2,137.50	\$412.50	\$545.47
Industrial	82	\$49,687.50	\$2,512.50	\$412.50	\$605.95
Public Health	12	\$14,325.00	\$3,862.50	\$637.50	\$1,193.75
Public Water Supply	2	\$825.00	\$412.50	\$412.50	\$412.50
Haz. Waste TSD	10	\$7,987.50	\$1,500.00	\$525.00	\$798.75
Landfill	1	\$2,512.50	\$2,512.50	\$2,512.50	\$2,512.50
All Labs	532	\$437,625.00	\$3,865.50	\$412.50	\$822.60
Out-of-State Labs*	85	\$132,750.00	\$3,375.00	\$675.00	\$1,561.76
Wisconsin Labs*	447	\$304,875.00	\$3,862.50	\$412.50	\$682.05
Reciprocity Labs*	14	\$15,750.00	\$1,125.00	\$1,125.00	\$1,125.00

*These labs are included in the totals above.



LabNotes - Fall 1998
Volume 13, Issue 2
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